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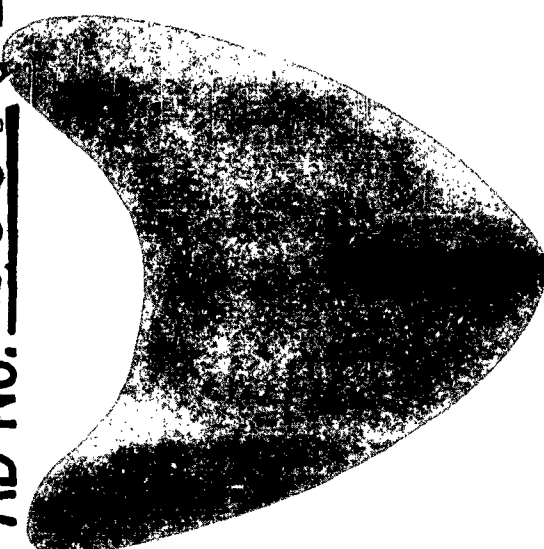


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SECOND QUARTER
JANUARY 1963

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**ELECTROLYTIC NIOBIUM
AND
NIOBIUM ALLOY CAPACITORS**

**KEMET DEPARTMENT
LINDE COMPANY**

DIVISION OF



CORPORATION

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RESEARCH AND DEVELOPMENT WORK ON ELECTROLYTIC NIOBIUM
AND NIOBIUM ALLOY CAPACITORS OF WET AND SOLID TYPES

BUREAU OF SHIPS CONTRACT NObsr-87478

SECOND QUARTERLY PROGRESS REPORT

OCTOBER 1, 1962 - DECEMBER 31, 1962

ELECTROLYTIC NIOBIUM AND NIOBIUM ALLOY CAPACITORS

OF WET AND SOLID TYPES

BUREAU OF SHIPS CODE 691A2

SUBJECT:

BuShips Contract NObsr-87478

Quarterly Research and Development Report, October 1, 1962 - December 31, 1962

REFERENCE

Project Serial No. SR-0080302 ST 9600

PROGRAM OBJECTIVES:

The development of 35, 50 and 100 volt niobium electrolytic capacitors of highest possible capacitance values, capable of full voltage operation at 85°C and with design objectives as listed in Military Specification MIL-C-26655 for:

- (1) electrical parameters,
- (2) environmental characteristics,
- (3) spatial configuration and dimensions,
- (4) operating temperature range (-65°C to +85°C)

Report written by:

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Development Laboratory
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Cleveland, Ohio

FOREWORD

A Pert Plan (Program Evaluation Review Technique) has been drawn up, in which the project has been divided into three separate tasks:

Task A: Work on niobium and niobium alloy sintered anode capacitors of solid and wet types

Task B: Work on niobium and niobium alloy foil capacitors of wet type

Task C: Basic studies of tantalum and niobium single crystals and foils

This plan has proved to be useful in assessing and controlling the progress of the various phases of the program. The Pert activity breakdown under each task is employed in the following progress report, although only the activities on which work has been started are listed.

SUMMARY OF PROGRESS

TASK A

Activity 1 - Exhaustive Trace Impurity Analysis of Niobium Materials Made by Three Different Processes (Union Carbide Metals Company)

Material 1 - niobium granules made by hydrogen reduction of pentachlorides

Material 2 - niobium granules made by carbothermic reduction of pentoxides

Material 3 - niobium slabs made by a proprietary process

A. Objective

It is expected that a co-ordinated analytical and electrical evaluation of these materials will help to identify the impurities mainly responsible for degradation of dielectric Nb₂O₅ films and thus serve as a guide for the subsequent purification studies of Activity 6.

B. Status

Materials 2 and 3 have been reduced to powder and final analyses are nearly complete. Material 1, however, has been found to be extremely difficult to grind, and work is continuing to find a suitable means of reducing this type of niobium to a fine powder.

Embrittlement of niobium by cooling from a temperature of 850°C, at a rate of 50°C per hour in a hydrogen atmosphere, resulted in the following hydrogen contents for the subject materials:

Material 1	0.64 weight % H
Material 2	0.86 weight % H
Material 3	0.68 weight % H

Material 2, with the highest hydrogen content, could be ground readily; on the other hand, although materials 1 and 3 showed essentially the same hydrogen content, only the latter could be processed to powder without unduly laborious milling and without the production of an undesirably large fraction of ultra fines. Further attempts are being made to raise the hydrogen levels in material 1, by variations in the treatment.

The results of chemical analyses completed to date are given in Tables 1A and 1B. As indicated in Table 1A, each material was sampled in the "as received" condition and a preliminary analysis conducted. Partially complete analyses on the final milled powders (100 mesh size and smaller) are also tabulated for materials 2 and 3. Further values for Li, Sn, V and Ti will be included in the next report. Table 1B lists other elements, which were looked for, but not detected qualitatively, in the three niobium materials.

It has been found necessary to develop special analytical methods for elements such as Li, Sn, V, Ti and Zr, for concentrations in the low parts per million range, since existing techniques are not sufficiently sensitive. Other elements which may require improved methods include Mo and Si.

Approximately five pounds of each material in the form of hydrided 10 mesh and smaller granules, have been received at Kemet for electrical evaluation. Samples of materials 2 and 3 after grinding to -100 mesh powder are now also on hand. Some of these materials are presently being evaluated at Kemet. The final sample of material 1 will be submitted when the milling problem has been solved.

Activity 2 - Preparation of Niobium-Tantalum Alloys

A. Objective

Union Carbide Metals Company is to make five pound batches of five different alloy compositions (0, 25, 50, 75 and 100% niobium by weight) and convert them into capacitor grade powder. The alloys are to be analyzed for interstitial impurities as well as for homogeneity, and several pounds of each material submitted to Kemet for evaluation.

B. Status

Two compositions, 75% niobium -25% tantalum and 25% niobium -75% tantalum by weight, were chosen for preliminary work to prove the proposed powder metallurgical method for preparing alloy powders. The test scale chosen was 100 to 400 grams of powder, blended to the desired compositions.

The constituent powders used to prepare the blend were first milled to a nominal 200 M x D (i.e., 200 mesh size and smaller). Actually about 60% of the niobium powder and 98% of the tantalum powder was finer than 325 mesh. The elemental powders were then dehydrogenated at 700°C in vacuum before blending was carried out. The blended materials were compacted by isostatic pressing at 40 T.S.I. and sintered for 23 hours at 2000 to 2100°C in a vacuum of 0.02 μ Hg, to allow complete interdiffusion of the niobium and tantalum to take place.

The uniformity of alloying was then investigated metallographically and by use of an electron microscope. Each of the pilot alloys appeared homogeneous under microscopic inspection; and this was confirmed by the microprobe analyses, the results of which are given in Table II. It will be noted that good uniformity was obtained in each pilot alloy, and that in one case, the powder bar appeared more uniform than an arc melted sample of the same alloy. Since the homogeneity obtained with the powder metallurgy method is quite good, this procedure has been adopted for preparing the final five pound quantities of each alloy powder for electrical testing at Kemet. To complete the pilot alloy studies, the sintered bars were embrittled with hydrogen and milled to powder.

Data pertinent to the pilot evaluation were accumulated in some detail, since powder metallurgy data for niobium-tantalum alloys are not generally available. It should be stressed that the results presented in Table III are of a preliminary nature and that firm conclusions await further information from the work now in progress on the main quantities of alloys. Inspection of Table III indicates that the carbon content of both raw materials increased during milling. Since this is normally undesirable, precautions have been taken to insure against contamination during preparation of the larger quantities of alloys. Some pickup of oxygen and nitrogen apparently also occurred during milling under argon and during subsequent dehydrogenation. This is not considered serious in the case of oxygen, since subsequent vacuum sintering will reduce the oxygen content; and for nitrogen, the pickup was small. However, efforts are being made to minimize increases of O and N in future work.

The physical characteristics of the elemental powders were measured by determination of bulk densities and micromerograph particle size distributions. These data indicate that the tantalum powder was finer than the niobium powder - the majority of tantalum particles lay in the 10 to 50 micron size range, while the niobium powder distribution spread over a range from 10 to 70 microns.

Although no tests were made to optimize particle size distribution, the densities obtained for the pressed and sintered bars were quite high. A density of 9.1 gms/cc was obtained on the 25 weight % tantalum alloy, and this corresponds to 90% of the density of the arc melted portion of this alloy. If a correction is made for the 2% higher tantalum content of the melted button, the density of the sintered bar is about 92% of the theoretical value. Similarly, the density of 12.8 gms/cc determined on the sintered 75 weight % tantalum alloy represents about 93% of the probable true density for this composition.

A noteworthy effect of the 23 hour vacuum sintering at 2000-2100°C, and 0.01 to 0.02 μ pressure, is the marked reduction in carbon and oxygen levels. This is probably due not only to the $C + O \rightarrow CO$ reaction, but also to the evaporation of volatile metal oxides. Apparently the nitrogen level was also reduced. Confirmation of these results by further tests, conducted from a quantitative thermodynamic viewpoint, is desirable.

Analyses of the milled alloy powders are not yet completed. As mentioned previously, efforts were made to minimize contamination by atmospheric gases during processing. Niobium and tantalum lined mills, which were loaded in a leak-tight dry box, then O-ring sealed and removed for milling, have been used. The ball mills were allowed to cool before discharge of the contents, either in air (for relatively coarse powder) or in the argon dry box (for fine -325M powder).

The raw materials for all final alloys have now been prepared. The blended powders have been pressed into compacts which are presently in the process of being sintered, hydrided and reground to powder. Since several failures of furnace resistance heating elements have caused some lost time, the probable completion date for this activity will be about two weeks later than planned.

An additional experiment was performed, in which a mixed compact of niobium and tantalum oxide powders with carbon was reduced by thermal treatment. The resulting product was a nominal 5 weight % niobium-95 weight % tantalum alloy. Five pounds of this material, in roundel form, were delivered to Kemet for evaluation.

There, a 300 gram portion has been hydrided and milled to -100 mesh powder (approximately 92% -325 mesh) and dehydrided. A sample of this powder was then submitted for impurity analysis, while the remainder was blended and pressed into capacitor anodes. All details of blending, pressing and sintering were identical with those for a standard 100% tantalum high purity production material, against which a standard quality control powder evaluation was carried out. The details of this study are given in Table IV, from which it is clear that the alloy powder displayed markedly inferior electrical characteristics.

Activity 3 - Determination of Optimum Conditions for Removal of Carbon from Niobium

A. Objective

The object of this study at Kemet is to determine the efficacy of high temperature vacuum prepurification and oxygen predoping of niobium materials, in reducing the level of carbon in sintered anodes, thereby improving their electrical performance.

B. Status

Two different niobium materials have been processed through to the final electrical evaluation stage of the program represented by the flow diagram shown in Figure I.

The analytical results are presented in Table V, along with the results of breakdown tests conducted on a small number of plugs from the final groups represented by analyses C(10), C(11), C(12), C(13), C(14) and C(15) for each material.

For the analytical phase, carbon, oxygen and nitrogen were selected as the non-metallic contaminants most likely to be picked up during various processing operations and to be responsible for degradation of electrical performance of plugs pressed from the materials; similarly, iron was chosen as representative of the group of metallic impurities which are most likely removed mainly by volatilization during high temperature prefurnacing or sintering.

Some rather anomalous analytical results will be noted in the case of each material:

- (1) There was an apparent pickup of iron during the initial hydriding, milling and dehydriding (compare analyses C(1) and C(2) for iron) despite the use of niobium lined equipment, high vacuum or inert atmospheres, and the extreme care with which the materials were handled at all stages of treatment. Since this result has also been observed in previous studies, it is suspected to be caused by tramp iron already present in the material.

- (2) The large disparity in C, O, and Fe levels for samples C(4) versus C(8) and C(3) versus C(6) in each case is surprising, since these samples are representative of the material at the same stage of treatment. The comparative results for carbon and iron are particularly anomalous. The only explanation that can be advanced for these results is that, in each case, C(3) and C(4) represent 10 gram powder samples made from a few slabs for initial impurity analysis, whereas C(6) and C(8) were determined from 10 gram samples removed from the main batch of slabs after rendering into powder; thus, a small given amount of contamination introduced during H-M-D would cause a much more pronounced effect on the former samples than on the latter samples. However, since the same qualitative and quantitative effect was observed for both materials, although each was treated separately, this explanation is rather doubtful. Moreover, the consistency of nitrogen analyses for these samples makes the explanation even more difficult.
- (3) An attempt was made to oxygen dope all desired sub-batches of slabs to the same oxygen level (6000 ppm) by electrochemical formation of Nb_2O_5 , followed by diffusion of oxygen into the material. Unfortunately, the oxygen doping calculations were based on analytical results C(3) and C(4), since results C(6) and C(8) were not available at the time. Since the latter were more truly representative of the main batches of slabs, the doped samples represented by C(5), C(7) and C(9) show a spread in values from 8800 to 11,900 ppm oxygen. Moreover, samples C(9) of each material were treated together for oxygen dispersion and hydriding - since a slight temporary air leak occurred during this run, as evidenced by a tenfold increase in nitrogen levels, additional pickup of oxygen occurred.

C. Conclusions

- (1) A study of the analytical results indicates that a high temperature vacuum prepurification at 2300°C is somewhat more effective than a similar treatment at 2100°C in removal of carbon. However, the results for control groups C(14) and C(15) indicate that this prepurification treatment is not necessary to reduce the carbon level from as high as 550 ppm down to 20 ppm, provided the plugs receive a vacuum sinter at 2100°C. This conclusion needs further confirmation since the extent of carbon removal may be controlled by back diffusion of pump oils into the furnace chamber during sintering, despite elaborate baffling. A Vac-ion pumping system is presently being set into operation and it is hoped eventually to test out this possibility.

Similarly, although it appears that oxygen doping does not afford any marked improvement in carbon reduction, again the conclusion is tentative for the reason outlined above.

- (2) Correlation of the breakdown test results with the analytical results indicates that (see especially C(14)) a high nitrogen content in niobium materials may produce deleterious effects on plug quality. Similarly, iron (compare C(12) and C(13)) may exert some influence. Clearly the range of concentrations of the various impurities is not broad enough to delineate definitely their effects on breakdown voltage.
- (3) Larger batches of plugs from each group are currently being processed through to the canning stage for measurements of size factor, dissipation factor and leakage current. It is expected that these electrical measurements, along with subsequent life test data, will serve to identify more clearly the impurities most detrimental to electrical characteristics of the pentoxide film.

Activity 4 - Determination of Optimum Anodization Conditions for Niobium Anodes

A. Objective

The object of this work is to determine the best formation electrolyte and formation conditions (formation temperature, current density and time) for niobium capacitor anodes.

B. Status

A large batch of 0.118" x 0.230" long plugs, pressed from a powder blend consisting of 25% -200/325 and 75% -325 mesh material, (niobium powder A as described in Table IVa of the last quarterly report) sintered at 2100°C for 30 minutes and stored in argon, was used to test the thirteen electrolytes listed in Table VI. Evaluation of the electrolytes, the conductivities of which were adjusted to be approximately equal at 25°C in most cases, was based on:

- (1) Measurements of maximum formation voltage at 25°C and 90°C, for constant current densities of 5 mA/gram and 50 mA/gram.
- (2) Measurements of terminal leakage current at 100% of formation voltage, after two hours at formation voltage.

In the breakdown voltage tests, up to seven plugs were tested individually under each set of conditions (electrolyte, current and temperature). For the leakage current tests, small batches of plugs were formed to 150 volts at 25°C and a constant current density of 50 mA/gram. Wet test measurements of capacitance and dissipation were also carried out to check the anomalous behaviour exhibited by one class of electrolytes.

The results of the study are presented in Tables VIIA and VIIB. The most salient information obtained can be summarized as follows:

- (1) Although the voltage-time phenomena for constant current formation are rather complex, four general classes of characteristics could be distinguished, as illustrated in Figure II.

Curve A - typifies the v-t relationship for most electrolytes at 25°C and high current density. In this case the voltage rises linearly with time until a voltage is reached, beyond which the oxide layer either breaks down (B.D. as evidenced by large voltage scintillations) or begins to crystallize (as evidenced by a levelling off (L.O.P.) to constant voltage and a change from bright interference colours to a dull grey matte appearance).

Curve B - typifies the v-t relationship for most electrolytes at 90°C and high current density. In this case the voltage (and therefore the oxide thickness) increases linearly with time, until at a comparatively low voltage, the slope changes abruptly; at this L.O.P., crystallization of the oxide appears to start; and with further increases in time, the voltage rises very slowly.

Curve C - typifies the v-t relationship for most electrolytes at 25°C or 90°C and low current density. In this case the voltage increases linearly with time, but with a very low slope - if anodization is carried out for a long enough period, crystallization again starts at low voltages (~100 volts) as for curve B.

Curve D - typifies the v-t relationship at 25°C and 90°C and high current density, for electrolytes containing borate ions. In this case the behaviour is very peculiar and is characterized by a very rapid, non-linear increase of voltage with time. There is some evidence, such as the capacitance results for electrolyte VII in Table VIIB, that a different type of oxide is formed when borate electrolytes are used.

- (2) The role of the electrolyte in the formation is much more important than might be expected. The particular electrolyte used appears to influence not only the thickness of oxide attained before breakdown, but also the rate of build-up of oxide, as indicated by the (dv/dt) values listed in Table VIIA. Both very weak acids, (such as II, and V), and strong acids and bases, (such as IV and III), appear to be poor formation electrolytes. The best electrolyte characteristics appear to be provided by the medium strength acids, such as I, VI, VIII and XI.

C. Conclusions

Formation Electrolyte - electrolytes VI and XI appear to provide the best overall results.

Formation Temperature - Formation at 90°C appears to be undesirable because of a tendency for transition of the oxide layer from an amorphous structure to a crystalline structure at relatively low voltages, even in otherwise excellent formation electrolytes. Formation at 25°C or lower provides a good oxide layer - a fuller investigation should be carried out at 0°C, since the highest breakdown voltages were achieved at this temperature.

Formation Current Density - A low current density necessitates impractically long formation times to attain moderately high voltages. On the other hand, care must be exercised during formation at high current densities, in order to avoid localized overheating of the electrolyte near the plugs.

Formation Time - Figure III illustrates the results of a study of oxide stability with time under applied voltage for one of the best electrolytes. It is clear from this test that the leakage current continues to drop considerably for a long period of time after formation voltage is reached. Consequently, rather long formation times of four hours or more may be required to obtain optimum dielectric properties.

Activity 5 - Determination of Optimum Processing Conditions for Solid Niobium Plug Capacitors

A. Objective

The object of this work is to determine the best processing methods for the preparation of solid niobium capacitors up to the canning stage. Parameters to be studied in this phase include optimum particle shape and distribution, green density of plugs, sintering conditions, chemical etching, and reformation-impregnation conditions.

B. Status

(a) Sub-Activity 5.1 - Studies of the Effect of Sintering Temperature and Time on Electrical Characteristics of Anodes

Further work, carried out since the last report, has not changed the conclusions reached at that time: that a sintering temperature of 2100°C and sintering time of 30 minutes affords the best overall electrical characteristics.

(b) Sub-Activity 5.2 - Anode Cleaning and Storage Studies

The object of this work is to determine:

- (1) the effect of preformation and postformation chemical cleaning,
- (2) the effect of anode storage in air, argon, and demineralized water, on anode performance (leakage current and breakdown voltages of plugs).

Chemical Cleaning Studies

A niobium powder (material B described in Table IVa of the last quarterly report) consisting of 7% -100/+200, 44% -200/+325 and 49% -325 mesh material was used to press a batch of 0.118" diameter x 0.230" length plugs. The anodes, after sintering at 2100°C for 30 minutes, were stored in air in a glass container, prior to use in tests.

To study the effects of various chemical treatments, plugs were formed at 25°C in electrolyte I (Table VI) to 150 volts at a constant current density of 50 mA/gram. Since a chemical etch of sintered anodes was expected mainly to improve leakage current characteristics, attention was directed to measurements of terminal leakage current and of breakdown voltages obtainable. However, in certain cases, capacitance and dissipation factor were also measured, using methods described in a previous report.

Six batches of 5 plugs each were treated in the following ways:

- (1) Plugs were soaked in acetone, then washed in boiling demineralized water prior to formation.
- (2) Plugs were etched for 1 hour in a 10% bromine-methanol solution, then washed and anodized to breakdown.
- (3) Plugs were anodized to 100 volts, washed, then etched in bromine solution for 1 hour, washed again and anodized to breakdown. A control batch was treated identically except for etching.
- (4) Formation to 100 volts was followed by a wash, an etch in bromine solution for three hours, another wash and then formation to breakdown.
- (5) Anodization to 150 volts was followed by a 1 hour etch in bromine solution with the usual washing cycle before and after the etch, and then formation to breakdown.

The results of this study are summarized in Table VIII. It will be noted that treatments (1) and (3) resulted in the highest breakdown voltages. A combination of these two techniques may be even more useful, but has not yet been tried. On the other hand, it is also evident that a prolonged etch in bromine, as in (4), leads to inferior results. This indicates that a slight bromine attack on the oxide layer during an extended exposure, may offset the beneficial effects of leaching impurities out of the dielectric layer.

Storage Studies

A blend of 25% -200/325 and 75% -325 mesh size niobium powder (material A of Table IVa in the last quarterly Report) was used to press 0.118" x 0.230" plugs, which were sintered at 2100°C for 30 minutes. After sufficient cooling in the high vacuum furnace, the vacuum was broken with argon. The sintered batch was then divided up, some plugs being stored in air, others in distilled water, and the rest in a dessicator which was partially exhausted to about 20 microns pressure and filled with argon. When anodes were withdrawn from the dessicator prior to anodization tests, one group was immersed in water, and another group exposed to air for a maximum length of time of 24 hours.

To compare the effect of the various storage methods for sintered anodes, the parameters chosen for evaluation were again size factor, dissipation factor, terminal leakage current and maximum breakdown voltage. The formation conditions and method of measurement were the same as used in evaluating the effects of various chemical treatments. For leakage current measurements ($V_F = 150$ volts) at least ten plugs were tested in each case, while for breakdown voltage tests, a minimum of five plugs were tested individually.

The results are summarized in Table IX. Although there is some discrepancy between terminal leakage current and breakdown voltage results, it is evident that the preferred method of storage is in demineralized water. The importance of breaking vacuum with argon instead of air, after sintering of anodes, cannot be assessed from the present work, since all plugs used in the study were from the one batch for which vacuum was broken with argon. A further study should be carried out to check this point and also to substantiate the present conclusions.

(c) Sub-Activity 5.3 - Determination of Optimum Particle Size Distribution for Niobium Powders used in Pressing Capacitor Anodes

Many variations are possible at the primary stage in the development of porous capacitor anodes, such as (1) niobium raw material selection (2) powder preparation and cleaning (3) powder particle size distribution and particle shape chosen for the anodes (4) pressing and sintering parameters.

Although some aspects of this process are also covered under other activities, it is clear that, for proper correlation of results, it is necessary to formulate a basic study in which as many as possible of these variables are investigated on one given material.

The present program consists in making plugs with 16 different variations in powder preparation and processing, as outlined in the flow diagram of Figure IV and in Table X. A five pound lot of niobium, made by carbothermic reduction of oxide roundels, was chosen as the raw material. All reductions in powder particle size are performed by ball milling under argon in a niobium lined mill.

The effects of prefurnacing at 2200°C on the purity and milling characteristics of the powder is under investigation by study of -400 mesh powder in both as-received and prefurnaced conditions. The influence of particle size on electrical properties is considered through evaluation of the prefurnaced powders in three ranges: 100% -200/325 mesh, 25% -200/325, 25% -325/400 and 50% -400 mesh, and a 100% -400 mesh powder.

Two powder cleaning methods are under test:

- (1) Cleaning in 30% HNO_3 followed by removal of "fines" (particles of less than 1 micron diameter) by screening in demineralized water.
- (2) Etching in 10% bromine-methanol solution followed by a thorough washing in boiling demineralized water.

The powders cleaned by method (1) are pressed to three different green densities - minimum density and minimum +0.75 and 1.5 grams/cc; while the powders cleaned by method (2) will be evaluated at the middle density only. All powder preparations in the eight variations described have been completed and also the pressing and sintering of the 16 different groups of plugs required. The plugs, all nominally 0.160" in diameter x 0.25" long, were sintered at 2000°C for 30 minutes and stored in demineralized water in covered polyethylene containers prior to testing.

The densities and dimensions of the powders and sintered anodes are listed in Table XI. The Scott density measurement is an evaluation of powders through the density determination of loose powder reproducibly compacted in a controlled free fall into a container of known volume and weight. It is of interest to note that for the prefurnaced powders (designations II, III and IV in Table XI) the coarser materials have the higher Scott densities: for example, 43.9(2) gms/in³ for the -400 mesh powder versus 52.2(5) gms/in³ for the -200/325 powder. The bromine etch (B powders) slightly reduces the average size of the powder particles, as indicated by the lower Scott densities: 46.5(1) gms/in³ for etched powder versus 47.7(6) gms/in³ for powder cleaned in HNO_3 and screened. On the other hand, the as-received control powder (designation I in Table) does not conform to this pattern, since it displays higher Scott densities than either the -400 mesh (II) or the blend (IV) of the prefurnaced powders; similarly, its bromine etched sample is slightly denser than the sample cleaned in HNO_3 and screened (48.5(5) versus 48.0(2) gms/in³).

The results of the pressing and sintering of powders cleaned in HNO_3 are summarized in Figure V, which shows graphically the % increase in density during sintering as a function of "green" density. The data are consistent except for the blended powder (IV), which gave scattered results. As expected, the curves indicate that the higher the green plug density, the smaller the density increase during sintering. Also, the fine powders, (I and II) show greater increases during sintering than do the coarser blends (III and IV).

For example, for the same starting green densities (say 5.0 gm/cm^3), the coarser -200/325 mesh powder (III) increased 3% in density, whereas the fine -400 mesh powder (II) increased 9% in density. Finally, the plugs pressed from prefurnaced powder sintered to slightly lower densities than the plugs pressed from the as-received powder. (II and I in Figure V).

The eight powders are being further evaluated through:

- (1) Chemical analyses for H, O, N, C and Fe - samples have been submitted
- (2) Micromerograph analyses - samples have been submitted
- (3) Microscopic investigation including analysis of particle size distribution using a Zeiss particle size analyzer - photographs of various powders have been taken for this work.
- (4) Surface area measurements - the Sorptometer equipment required for this phase is expected to arrive in January, 1963.
- (5) Further sub-classification of the -400 mesh powder size distribution by an air stream flotation method, using an "Infrasizer".

The 16 groups of sintered anodes are to be evaluated as follows:

- (1) Microscopic studies of sintered and anodized plugs
- (2) Breakdown voltage tests at 25°C in electrolyte I
- (3) Wet tests of terminal leakage currents and of capacitance and dissipation factor at 120 and 1000 cps, on anodized plugs
- (4) Processing of anodes into solid capacitors followed by electrical evaluation and life testing.

When all the results are available, a thorough attempt will be made to correlate electrical properties of anodes with the powder evaluation results and plug pressing parameters. The more promising methods will then be applied to other niobium materials, to a comparison of micro-pulverized powder with ball milled powder, and to a more detailed study of sintering conditions.

(d) Sub-Activity 5.5 - Determination of Optimum Impregnation and Reformation Methods

For the first phase of this program, as outlined in the flow diagram of Figure VI, the parameters under study are dip/reformation sequence and pyrolysis temperature.

A batch of 0.160" diameter x 0.300" long plugs has been pressed from a powder blend (niobium material B) consisting of 4.3% -100/200, 18.8% -200/325 and 76.9% -325 mesh material, sintered at 2100°C for 30 minutes and stored in demineralized water.

The initial evaluation of anode quality (Test II.3 of Figure VI) has been completed along with the preliminary investigation of possible thermal damage to the dielectric layer during pyrolysis (Test II.3 of Figure VI).

The results of this test, summarized in Table XII, indicate that subjection of the anodes to 300°C for short periods causes some change in the dielectric layer, as evidenced by an increase in both capacitance and dissipation factor - on the other hand, the leakage currents are apparently reduced by this treatment.

Work has been started on Tests III.1 and III.2. Test III.1 comprises an estimate of the number of $\text{Mn}(\text{NO}_3)_2$ dips, N_0 , required to produce saturation of the plug pores with MnO_2 , as a function of pyrolysis temperature. The MnO_2 content is being determined both by a method of weighing and by a measurement of total manganese content. Test III.2 involves a study of the effect of pyrolysis temperature and dip/reformation sequence on electrical properties of canned anodes.

Other parameters which will be investigated in subsequent phases include studies of optimum reformation conditions and of methods of chemical impregnation of plugs with semiconducting material, in place of the dip-pyrolysis technique.

Activity 6 - Preparation of Highly Purified Niobium Powders

A. Objective

After the three materials described under Activity 1 have been analyzed and evaluated, a process will be selected by which the important impurities can be removed. It is planned to add certain impurities deliberately in order to determine their effect upon the electrical properties of anodized films.

It is also planned to evaluate another type of high purity niobium material, in the form of microspheres of a selected particle size distribution.

B. Status

In an initial tentative purity specification, it has been decided to consider reduction of levels, in Activity 1 materials, of the following impurities:

1 p.p.m. maximum
titanium

10 p.p.m. maximum
iron, tungsten, vanadium,
silicon, molybdenum,
silicon, nitrogen

The first phase of this program, involving the development of analytical methods for very low part per million concentrations of these elements, is currently under investigation within Activity 1.

Bench scale investigations of liquid extraction and ion exchange procedures, to chemically remove the undesirable impurities from niobium-rich solutions, are also being started.

Four pounds of 0.063" diameter niobium wire, produced from high purity electron beam melted material, have been packed under argon at Haynes Stellite Company and shipped to Linde Crystal Products Department for preparation of microspheres.

Activity 9 - Determination of Optimum Fill Electrolyte for Wet Plug Capacitors Determined

A. Objective

The object of this phase is to determine the best operating electrolyte for wet capacitors with regard to compatibility with the dielectric, range of temperature operation, and dissipation factor.

B. Status

The work of determining the best fill electrolyte for pure niobium sintered anodes, under sub-activity 9.1, was started in December and will continue during January 1963.

Since most of the promising electrolytes are highly corrosive, it was also necessary to begin selection of compatible components (e.g., teflon and rubber) and development of adequate sealing techniques. The following necessary processing equipment is presently in various states of completion:

- (1) an electroplating assembly for platinization of the interior of silver capacitor cans.
- (2) a jig for soldering the negative terminal leads to the bottom of the capacitor cans.
- (3) sealing equipment for swaging of lead wires, for spinning seals onto the lead wires, and for spinning the silver cans around the insulating assembly to obtain a liquid-tight seal.
- (4) a butt-welding fixture for attaching solderable lead wires to the positive niobium lead.

TASK B

Activity 1 - Preparation of Pure Niobium Foil

A. Objective

Haynes Stellite Company is to prepare ten pound quantities of high purity 0.050" niobium sheet by melting and rolling of two different materials:

Material 1 - electron beam purified niobium from Haynes

Material 2 - Parmec niobium from Parma Research Laboratories
Quantities of each material are to be rolled down to 0.010" sheet and samples supplied to Kemet for electrical evaluation and to Union Carbide Metals Company for impurity analysis.

B. Status

The prepurification work has been completed and sample quantities of each material have been received at Kemet in four different metallurgical conditions:

- (1) strained foil - as rolled
- (2) stress relieved foil - approximately 60% recrystallized after heat treatment at 980°C for 1 hour
- (3) recrystallized foil of smallest grain size - 100% recrystallized to grain size ASTM No. 6 after heat treatment at 1200°C for 1 hour
- (4) recrystallized foil of smallest grain size (ASTM No. 6), pack rolled between niobium cover plates to minimize surface contamination.

Samples of each material have also been submitted for impurity analysis.

Activity 2 - Preparation of Five Different Niobium-Tantalum Alloys

A. Objective

Haynes Stellite Company is to prepare four pound lots of five different alloys of tantalum with niobium (0, 25, 50, 75 and 100% tantalum by weight) by electron beam melting of high purity materials. Two pound quantities of each alloy are to be supplied to Kemet in the form of recrystallized 0.010" foil, for electrical evaluation. Samples are also to be submitted for impurity and homogeneity analysis at Union Carbide Metals Company.

B. Status

The raw materials have been obtained and charges weighed out for compaction to pressed bars, of all five alloys. The starting materials are high purity tantalum powder prepared from electron beam melted ingots and 10 MXD niobium powder from Union Carbide Metals Company. The compacts are presently being double electron-beam melted into ingots, which will then be processed into 0.010" thick strip. The preparation is expected to be completed early in February 1963.

Activity 3 - Preparation of Niobium-Platinum and Niobium-Zirconium Alloys

A. Objective

Four pound lots of the following niobium alloys are to be made at Haynes Stellite Company, by electron beam melting of suitable pure constituent materials:

- (1) Niobium - 0.1 weight % Platinum alloy
- (2) Niobium - 1.0 weight % Zirconium alloy

Two pound quantities of each material are to be supplied to Kemet in the form of recrystallized 0.010" foil for electrical evaluation. Samples are also to be submitted for impurity and homogeneity analysis at Union Carbide Metals Company.

B. Status

The niobium -1.0% zirconium alloy has been prepared and a sample supplied to Kemet in the form of 0.010" thick sheet, after vacuum annealing for 1 hour at 1370°C. A sample has been submitted for analysis.

Preparation of the niobium -0.1% platinum alloy, now under way, is scheduled for completion some time in February 1963.

Activity 4 - Determination of Optimum Processing Conditions for Niobium and Niobium Alloy Foils

A. Objective

The objective of this work is to determine the best metallurgical, chemical cleaning and anodization processes for pure niobium foil and for the various alloys described in the preceding sections.

B. Status

Work was started in December on the study of optimum anodization conditions (formation electrolyte, temperature, current density, etc.) for pure niobium foil. This work, along with a similar program for alloys, will continue during the next quarter, at the end of which period it will be described in detail.

Activity 5 - Determination of Optimum Fill Electrolyte for Niobium and Niobium Alloy Foils

A. Objective

As in Task A Activity 9, the purpose of this work is to determine the best fill electrolyte from the standpoint of chemical activity, conductivity and range of temperature operation.

B. Status

Work on selecting a good fill electrolyte for wet niobium foil capacitors has been started and also on the associated problem of selecting compatible capacitor parts for seals, etc.

The following processing equipment is now being developed:

- (1) lead wire bending equipment
- (2) welding equipment for attaching leads to anode and cathode foils
- (3) a special formation tank for anodizing foils
- (4) foil winding machinery for assembling foil capacitors
- (5) sealing equipment
- (6) equipment for butt-welding solderable lead wires to the niobium foil leads

TASK C

A. Objective

The objectives of this work are:

- (1) To compare the properties of Ta_2O_5 and Nb_2O_5 films in order to determine whether one is intrinsically superior as a dielectric material.
- (2) To compare the dielectric properties of Nb_2O_5 films formed on polycrystalline foil, porous plugs and single crystal surfaces, in order to determine the role of grain boundaries in the formation of anodic film defects.

B. Status

X-ray analyses of 1 centimeter diameter cylindrical single crystals of tantalum and niobium (with the 100 planes perpendicular to the longitudinal axis) using the Schulz-Wei Zone reflection method, revealed a small number of low angle misorientations. Reference marks have been scribed on sections of the crystals so that the position of these sub-grain boundaries will be known during electrical testing. Two smaller diameter single crystals have also been obtained for this work. The results of a chemical analysis of these crystals are given in Table XIII.

A program has now been outlined and a concerted investigation under this task is scheduled to begin in January 1963, in which an attempt will be made to correlate electrical evaluation of Ta_2O_5 and Nb_2O_5 films with X-ray and electron microscopic examination. Of particular interest at present are:

- (1) the activation energies associated with the transition from the amorphous to the crystalline state.
- (2) the role of chemical defects (e.g., interstitial impurities) and physical defects (e.g., scratches) in such phenomena as crystallization and electrical breakdown.
- (3) An examination of anodic films formed in a "good" and in a "poor" electrolyte, to uncover possible differences in structure.

TABLE I A
ANALYSES OF NIOBIUM FROM THREE DIFFERENT PROCESSES

MATERIAL	1 Hydrogen Reduced From Pentachloride		2 Carbon Reduced From Pentoxide		3 Proprietary Process		Detection Method
	As Recd.	H + M 100 M x D*	As Recd.	H + M 100 M x D*	As Recd.	H + M 100 M x D*	
ELEMENT, ppm: C	30		70	110	80		(1)
O	60		2800	2700	650	1500	(2)
H	71		620	7800	12	6600	(2)
N	3		120	237	25	43	(3)
B	0.4		0.4	0.2	0.5	0.3	(4)
Al	<40 ^a		<40	<30	<40 ^a	<30	(4)
Ca	<20		20	<30	<20	30	(4)
Cr	13		15	12	11	11	(5)
Co	<10		<10	< 2	<10	2	(5)
Cu	6		6	9	47	44	(5)
Fe	130		180 ^b	67	110	187	(5)
Mg	<20		<20	<30	<20	<30	(4)
Mn	< 5		< 5	< 5	< 5	< 5	(5)
Mo	4		34	36	4	-	(5)
Ni	15		8	-	21	22	(5)
Si	<50		<50	17	<50	130	(4)
Ta	730		970	1100	320	-	(5)
Ti	<20 ^a		25	-	<20 ^a	-	(4)
W	58		400	361	< 5	< 5	(5)
Zr	3		0.8	0.9	1	1.7	(6)
Sn	10		< 5		15		(5)

NOTES: H = Hydrided

M = Milled

a = Not detected.

b = Average of 4 analyses ranging from 90 to 300 ppm, indicating tramp iron.

Magnetic separation was made on the final powder.

* Nominal size.

Detection Methods: (1) Combustion Conductometric; (2) Vacuum Fusion;

(3) Distillation-Spectrophotometric; (4) Emission Spectrographic;

(5) Spectrophotometric; (6) Extraction-Emission Photometric.

TABLE I B

OTHER ELEMENTS SOUGHT BUT NOT DETECTED IN ANY OF THE NIOBIUM MATERIALS

Element	Estimated Detection Sensitivity ppm	Element	Estimated Detection Sensitivity ppm
Sb	20	Au	10
Ba	10	In	5
Bi	20	Pt	50
Cd	10	K	2
Ce	500	Pb	5
Cs	10	Os	50
Ga	3	Pd	10
Ge	5	Zn	100

TABLE II

ELECTRON BEAM MICROPROBE RESULTS FOR NIOBIUM-TANTALUM ALLOYS

Nominal Alloy Composition Weight %	% Tantalum			Standard Deviation	Number of Determinations
	Average	High	Low		
25% Nb - 75% Ta	76.8	79.8	74.5	1.4	20
75% Nb - 25% Ta	26.2	27.1	23.8	0.78	14
75% Nb - 25% Ta*	28.3	29.9	26.8	1.04	16

* A portion of the sintered alloy was arc-melted four times for comparison with the sintered bar.

TABLE III

SUMMARY OF DATA ON PILOT POWDER METALLURGY ALLOYS

<u>RAW MATERIALS</u>			
<u>As Received</u>		<u>Niobium</u>	<u>Tantalum</u>
Analysis, ppm:	C	80	160
	O	2700	2000
	H	-	-
	N	130	90
<u>Hyd. + Mill. 200 M x D</u>			
Analysis, ppm:	C	220	590
	O	3800	2700
	H	1500	3500
	N	-	-
<u>200 M x D, Dehyd.</u>			
Analysis, ppm:	C	250	600
	O	4100	2900
	H	10	13
	N	190	120
<u>Scott Density, g/in.³</u>		<u>57.5</u>	<u>107.5</u>
<u>Micromerograph, μ</u>	<u>5</u>	<u>0.5%</u>	<u>4%</u>
<u>Distribution (in %)</u>	<u>5/10</u>	<u>1.5</u>	<u>5</u>
	<u>10/20</u>	<u>11.0</u>	<u>23</u>
	<u>20/30</u>	<u>17.0</u>	<u>30</u>
	<u>30/40</u>	<u>16.0</u>	<u>25</u>
	<u>40/50</u>	<u>17.0</u>	<u>13</u>
	<u>50/60</u>	<u>20.0</u>	<u>0</u>
	<u>60/70</u>	<u>17.0</u>	<u>0</u>

PILOT ALLOYS

<u>Blend 200 M x D</u>			
<u>Dehyd. Powders</u>		<u>75 Wt. % Nb - 25 Wt. % Ta</u>	<u>25 Wt. % Nb - 75 Wt. % Ta</u>
Analysis, ppm:	C	336	513
	O	3810	3200
	H	-	-
	N	172	138
<u>Scott Density, g/in.³</u>		<u>67.1</u>	<u>91.5</u>
<u>Pressed, 40 TSI</u>			
<u>Density, g/cc.</u>		<u>8.0</u>	<u>10.45</u>
<u>Pressed, Sintered in Vacuum, 2000-2100°C</u>			
Analysis, ppm:	C	150	60
	O	200	300
	H	10	17
	N	10	10
<u>Density, g/cc.</u>		<u>9.1</u>	<u>12.8</u>
<u>Sintered, Hydrogenated, Milled</u>			
Analysis, ppm:	C		
	O		
	H	870	
	N		
<u>Size</u>		<u>71% -200 mesh</u>	

TABLE IV

QUALITY CONTROL TEST OF 5% NIOBIUM-95% TANTALUM ALLOY
AGAINST A STANDARD PRODUCTION CAPACITOR GRADE TANTALUM MATERIAL

Material	5% Nb-95% Ta Alloy	Tantalum, Lot 1865 Standard Blend WR
Sintered Density of Plugs ρ_s (grams/cc)	10.8	10.6
Average Breakdown Voltage on Wet Test $V_{B.D.}$ (Volts)	210	300
Charge Number on Wet Test Λ ($\mu\text{c}/\text{gram}$)	2040	1875
Average Capacitance (Solid Test) C (μf)	34.2	34.1
Average Leakage at 35 Volts (Solid Test) I_L (μa)	1.12	0.041
Average Dissipation Factor on Solid Test D (%)	11.2	3.1
Impurity Analysis of Sintered Anodes C and O Levels in p.p.m. by Weight	40, 2800	240, 2500

TABLE V

ANALYTICAL RESULTS FOR TWO NIOBIUM MATERIALS

AT THE VARIOUS STAGES OF PROCESSING OF ACTIVITY 3 (FLOW DIAGRAM OF FIGURE 1)

Sample Number	Impurity Analysis (Parts Per Million)								Average Breakdown Voltage*	
	UCM Lot BM 812				UCM Lot 2121				Volts	
	C	O	Fe	N	C	O	Fe	N	UCM Lot BM 812	UCM Lot 2121
C (1)	150	2,500	10	160	500	2,500	30	190	*Each average is for three plugs tested individually at 25°C and a current density of 50 ma/gm in proprietary electrolyte Y ₁	
C (2)	140	5,000	50	-	550	5,500	70	-		
C (3)	90	3,400	10	230	150	3,900	10	510		
C (4)	90	2,500	10	200	130	2,300	10	580		
C (5)	30	9,900	60	250	40	9,500	60	500		
C (6)	20	4,100	40	210	40	4,900	70	500		
C (7)	30	10,000	70	210	30	8,800	80	330		
C (8)	30	3,800	50	220	50	5,200	30	170		
C (9)	140	11,900	120	2,300	550	10,600	120	2,900		
C (10)	30	5,400	30	340	30	5,400	40	480	331	334
C (11)	20	3,400	20	270	20	4,200	20	400	335	347
C (12)	20	5,500	50	290	30	5,200	40	400	351	338
C (13)	20	3,000	30	240	20	4,000	10	330	351	344
C (14)	30	6,500	40	860	30	6,000	20	710	333	318
C (15)	30	4,100	20	220	30	3,600	20	440	366	346

TABLE VI
FORMATION ELECTROLYTES UNDER STUDY IN ACTIVITY 4

Code Number	Electrolyte	Composition	Conductivity at 25°C (ohm-cm) ⁻¹ × 10 ⁴	Conductivity at 90°C (ohm-cm) ⁻¹ × 10 ⁴	Appraisal as a High Voltage Formation Electrolyte
I	H ₃ PO ₄	Phosphoric Acid Demineralized Water	3.41	5.64	Good
II	COOH(CH ₂) ₂ COOH	Succinic Acid Demineralized Water	3.40	6.04	Poor
III	KOH	Potassium Hydroxide Demineralized Water	3.38	7.57	Poor
IV	HNO ₃	Nitric Acid Demineralized Water	3.41	5.30	Poor
V	CH ₂ (COOH) ₂	Malonic Acid Demineralized Water	3.42	5.17	Poor
VI	Y ₁	Proprietary	3.46	7.57	Excellent
VII	Borcol	Borax Ethylene Glycol	3.35	19.1	?
VIII	Phenacid A	Phenol Phosphoric Acid Demineralized Water	3.40	7.69	Good
IX	Phenacid B	Phenol Phosphoric Acid Demineralized Water	Not Miscible	3.70	Poor
X	CH ₃ COOH	Acetic Acid Demineralized Water	3.46	6.19	Poor
XI	Y ₂	Proprietary	1.38	2.58	Very Good
XII	Y ₃	Proprietary	14.9	26.3	Very Good
XIII	Borax	Sodium Borate Demineralized Water	11.5	33.7	Poor

TABLE VII A

ELECTRICAL BREAKDOWN AS A FUNCTION OF FORMATION ELECTROLYTES
AND OF FORMATION TEMPERATURE

Formation Current Density 50 ma/gram

Electrolyte Temp. During Formation	25°C				90°C				
	Electrolyte Number	Curve Type*	B.D.** or L.O.P.	Avg. B.D. or L.O.P. Volts	Slope dv/dt Volts/min.	Curve Type*	First L.O.P. Volts	Time to Reach Voltage V	
								V (Volts)	t (Mins.)
I	A	B.D.	268	3.20	B	84	150	335	
II	A	L.O.P.	137	2.83	-	-	-	-	
III	A	L.O.P.	141	2.96	-	-	-	-	
IV	A	L.O.P.	125	3.06	-	-	-	-	
V	A	L.O.P.	163	2.87	-	-	-	-	
VI	A	L.O.P.	431	3.45	B	126	158	305	
VII	D	L.O.P.	318	(12.0)***	D	300 Final L.O.P.	300	200	
VII	A	B.D.	252	3.14	B	88	140	190	
IX	-	-	-	-	B	98	146	300	
X	A	L.O.P.	129	2.80	-	-	-	-	
XI	A	L.O.P.	422	3.26	A	130 Final L.O.P.	130	50 ($\frac{dv}{dt}=2.60$)	
XII	A	L.O.P.	388	2.82	B	98	160	330	
XIII	D	L.O.P.	168	(3.43)***	-	-	-	-	

* See Figure II for Curve Types.

** B.D. = Breakdown; L.O.P. = Leveling Off Point.

*** Effective Average dv/dt.

TABLE VII B

ELECTRICAL EVALUATION OF FORMATION CHARACTERISTICS (Contd)

Electrolyte Temperature	25°C		90°C		0°C	
Formation Current Density	5 ma/gram		5 ma/gram		50 ma/gram	
Electrolyte	Curve Type	Slope dv/dt Volts/min.	Curve Type	Slope dv/dt Volts/min.	Curve Type	L.O.P. Volts
I	C	0.36	-	-	-	-
III	C	0.33	-	-	-	-
VI	C	0.30	C	0.33	A	508 (dv/dt=2.67)
VII	(D+C)*	(0.90)	(D+C)*	(0.46)	D	350 (dv/dt=10.3)
XI	C	0.27	C	0.29	-	-
XII	C	0.33	C	0.22	-	-
XII	(D+C)*	(0.35)	-	-	-	-

* Small initial rise characteristic of curve D followed by slow linear rise with time characteristic of curve C.

Electrolyte Temperature 25°C, Formation Current Density 50 ma/gram				
Electrolyte Number	Formation Voltage V _F (Volts)	Avg. Terminal** Leakage Current I _L (ua)	Average Capacitance C (uf)	Average Diss. Factor D (%)
I	150	100	4.51	1.0
VI	150	125	4.45	1.0
VII	100	600	21.4	4.3
VII	125	570	19.4	4.4
VII	150	107	31.2	8.1
VII	250	164	31.0	8.4
VII	124*	196	19.0	4.9
VIII	150	150	4.54	1.1
XI	150	146	4.54	1.1
XII	150	112	4.51	1.1

* Formed to 90°C to equivalent of 150 volts at 25°C.

** Leakage measurements at formation voltage after 2 hours at voltage.

TABLE VIII

EFFECT OF ETCHING UPON ELECTRICAL PERFORMANCE OF NIOBIUM CAPACITORS

Material - Niobium Powder B						
Method of Preparation	Average Capacity μf	Average Diss. Factor %	Charge Number $\mu\text{c/gm}$	Size Factor mc/in^3	Average Terminal Leakage μa	Average Breakdown Voltage and Range Volts*
Soaked for 1 hour in acetone prior to anodization.	5.03	1.11	2930	268	168	284 (287-279)
Etched for 1 hour in 10% bromine solution prior to anodization.	5.01	1.06	2920	267	164	242 (246-238)
Anodized to 100 volts then etched in 10% bromine solution for 1 hour.	-	-	-	-	-	282 (295-267)
Same, no etch.	-	-	-	-	-	259 (277-238)
Anodized to 100 volts then etched in 10% bromine solution for 3 hours.	5.00	1.05	2920	266	172	227 (232-223)
Anodized to 150 volts then etched in 10% bromine solution for 1 hour.	4.87	1.12	2840	259	110	262 (267-257)

* Number of plugs averaged: 5

Leakage measurements at 25°C in Electrolyte I after 2 hours at formation voltage.

Sintering Conditions: 2100°C for 30 minutes.

Sintered Density of Anodes: 5.57 gm/cm³.

TABLE IX

STUDY OF OPTIMUM STORING CONDITIONS

Material - Niobium Powder A (25% -200/325, 75% -325 mesh)

Method of Storing	Average Capacity μf	Average Diss. Factor %	Charge Number $\mu\text{c/gm}$	Size Factor mc/in^3	Average Terminal Leakage μs	Average Breakdown Voltage and Range (Volts)*
Stored in argon for 2 weeks, then exposed to air.	4.51	1.0	2630	242	100	177 (195-158)
Stored in air for 2 weeks.	4.50	1.2	2620	242	100	225 (238-205)
Stored in water for 2 weeks.	4.56	1.3	2660	245	140	278 (290-269)
Stored in argon for 2 weeks, then immersed in water.	4.61	1.4	2680	248	140	239 (258-222)

* Number of plugs averaged: 5

Leakage measurements at 25°C , $V_F = 150$ volts after 2 hours at voltage.

Sintering conditions: 2100°C for 30 minutes.

Sintered density of anodes: 5.63 gm/cm^3 .

TABLE X

VARIABLES IN THE FIRST INVESTIGATION OF NIOBIUM POWDER PREPARATION

Plug Designation	Prefurnacing	Cleaning	Sizing		Remarks
I-A-Y	No	A	-400 Mesh	Minimum	Control
I-A-Y	No	A	-400 Mesh	Minimum +0.75	Control
I-A-Z	No	A	-400 Mesh	Minimum +1.50	Control
I-B-Y	No	B	-400 Mesh	Minimum +0.75	Control
II-A-Z	Yes	A	-400 Mesh	Minimum	
II-A-Y	Yes	A	-400 Mesh	Minimum +0.75	
II-A-Z	Yes	A	-400 Mesh	Minimum +1.50	
II-B-Y	Yes	B	-400 Mesh	Minimum +0.75	
III-A-Z	Yes	A	200/325	Minimum	
III-A-Y	Yes	A	200/325	Minimum +0.75	
III-A-Z	Yes	A	200/325	Minimum +1.50	
III-B-Y	Yes	B	200/325	Minimum +0.75	
IV-A-X	Yes	A	Blend	Minimum	25% 200/325, 25% 325/400, 50% -400
IV-A-Y	Yes	A	Blend	Minimum +0.75	25% 200/325, 25% 325/400, 50% -400
IV-A-Z	Yes	A	Blend	Minimum +1.50	25% 200/325, 25% 325/400, 50% -400
IV-B-Y	Yes	B	Blend	Minimum +0.75	25% 200/325, 25% 325/400, 50% -400

LEGEND

Prefurnacing for 30 minutes at 2200°C.

A - Clean 30 minutes in 30% HNO₃, remove fines through "Water Screening", 3 minutes settling time.

B - Etch 60 minutes in 10% bromine in methanol and wash.

TABLE XI

DENSITIES AND DIMENSIONS OF NIOBIUM POWDERS AND PLUGS

Plug Designation	Scott Densities		"Green" Plug Characteristics				Sintered Plug Characteristics				Percent Increase In Density
	Grams/in ³	Grams/cm ³	Diam. cm	Length cm	Weight grams	Density gm/cm ³	Diam. cm	Length cm	Weight grams	Density gm/cm ³	
I-A-X	48.02	2.93	0.414	0.634	0.365	4.28	0.391	0.603	0.361	4.98	16.4
I-A-Y	48.02	2.93	0.414	0.628	0.439	5.20	0.400	0.608	0.432	5.65	8.7
I-A-Z	48.02	2.93	0.414	0.636	0.505	5.90	0.401	0.616	0.484	6.22	5.4
I-B-Y	48.55	2.96	0.414	0.624	0.432	5.14	0.396	0.608	0.428	5.71	11.1
II-A-X	43.92	2.67	0.414	0.634	0.342	4.01	0.383	0.592	0.338	4.96	23.7
II-A-Y	43.92	2.67	0.414	0.622	0.400	4.78	0.391	0.593	0.374	5.25	9.8
II-A-Z	43.92	2.67	0.414	0.627	0.459	5.44	0.393	0.606	0.426	5.80	6.6
II-B-Y	42.97	2.62	0.414	0.623	0.404	4.82	0.390	0.596	0.389	5.46	13.3
III-A-X	52.25	3.19	0.414	0.634	0.392	4.60	0.407	0.632	0.397	4.83	5.0
III-A-Y	52.25	3.19	0.414	0.629	0.470	5.55	0.411	0.626	0.468	5.63	1.4
III-A-Z	52.25	3.19	0.414	0.645	0.546	6.29	0.410	0.641	0.540	6.38	1.4
III-B-Y	50.91	3.10	0.414	0.626	0.449	5.33	0.411	0.623	0.446	5.40	1.3
IV-A-X	47.76	2.91	0.414	0.634	0.363	4.26	0.395	0.609	0.366	4.91	15.3
IV-A-Y	47.76	2.91	0.414	0.626	0.438	5.20	0.404	0.616	0.426	5.39	3.7
IV-A-Z	47.76	2.91	0.414	0.634	0.501	5.87	0.404	0.628	0.500	6.21	5.8
IV-B-Y	46.51	2.84	0.414	0.625	0.430	5.11	0.402	0.615	0.421	5.40	5.7

NOTE: Averages of four test results.

TABLE XII

IMPREGNATION - REFORMATION STUDIES:

TEST II.3 FOR THERMAL DAMAGE DURING PYROLYSIS AND SUBSEQUENT REHEALING

Average Breakdown Voltage 315 Volts (in Electrolyte VI at 25°C)

Plugs 0.160" diameter x 0.300" long, 2100°C, 30 min. Sintering,
Formation: Electrolyte VI, at 25°C, Current Density 50 ma/gm

Test Conditions		Formation at 150 Volts			Formation at 175 Volts			Formation at 200 Volts		
		X Heat in Air	Y Heat in Air	Z Heat in Vacuo	X Heat in Air	Y Heat in Air	Z Heat in Vacuo	X Heat in Air	Y Heat in Air	Z Heat in Vacuo
	$I_L - \mu a$ at 100% V_F	600	540	540	320	300	240	300	320	330
After 2 Hours at Formation Voltage	$I_L - \mu a$ at 75% V_F	7	6	7	7	8	11	9	9	8
	$C - \mu f^*$	12.3	-	-	10.4	-	-	8.9	-	-
	DF - %	1.5	-	-	1.2	-	-	1.2	-	-
After 20 Min. Prior to Heat Treatment	$I_L - \mu a$ at 100% V_F	210	250	192	300	200	124	170	164	118
After 30 Min. After Heat Treatment	$I_L - \mu a$ at 100% V_F	138	164	250	110	132	174	100	108	170
	$I_L - \mu a$ at 75% V_F	5	6	7	5	6	6	17	10	8
	$C - \mu f$	12.3	12.5	12.0	10.8	10.8	10.2	9.7	9.6	9.4
	DF - %	1.5	1.5	1.3	1.7	1.7	1.4	2.1	1.9	1.6

* Capacitance and Dissipation Factor were Measured in 30% H_2SO_4 Solution at 25°C, 12 Volt DC Bias after 5 Minutes.

TABLE XIII

CHEMICAL ANALYSIS RESULTS FOR TANTALUM AND NIOBIUM SINGLE CRYSTALS

Material	Tantalum	Niobium
Description	$\frac{1}{8}$ " diameter x $\frac{1}{4}$ " long Electrochemically polished in HF + H ₂ SO ₄ + HC ₂ H ₃ O ₂	$\frac{1}{8}$ " diameter x $\frac{1}{4}$ " long Chemically cleaned in HF + HNO ₃
Analysis (ppm)		
O	4.6	140
C	3.5	4.9
Mo	100	100
Nb	100	-
Fe	100	100
Mn	100	-
Cu	1	-
Mg	-	1
Al	100	-

**FLOW DIAGRAM FOR TREATMENT OF A NIOBIUM MATERIAL
TO STUDY OPTIMUM PROCESSING FOR REMOVAL OF CARBON**

State

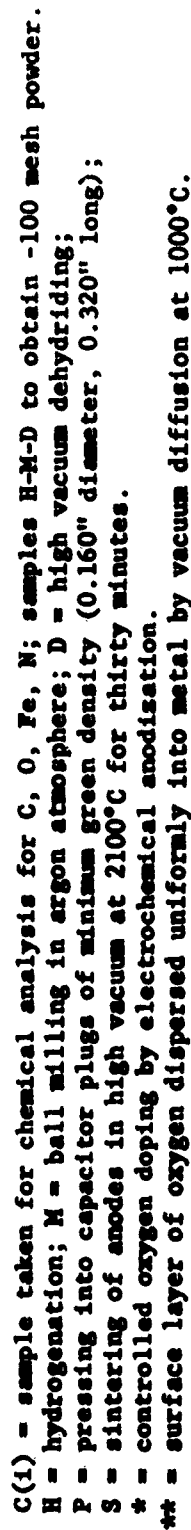


FIG. II
CHARACTERISTIC CONSTANT CURRENT FORMATION CURVES
UNDER VARIOUS CONDITIONS

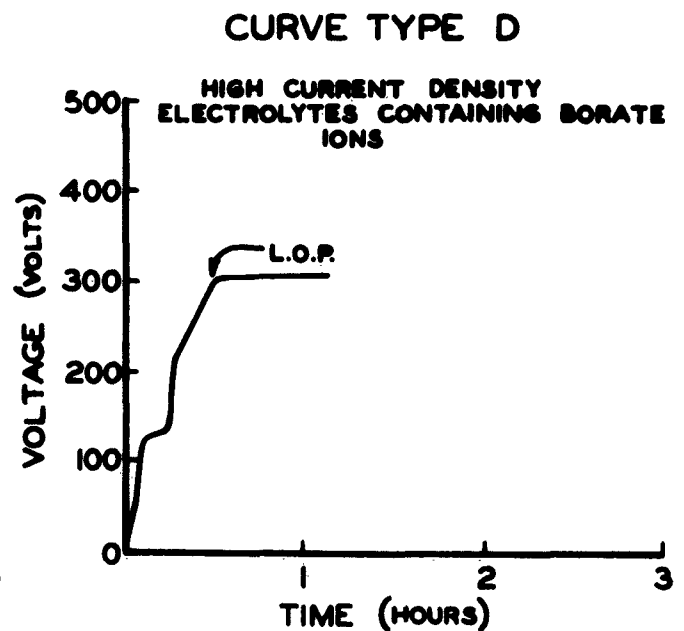
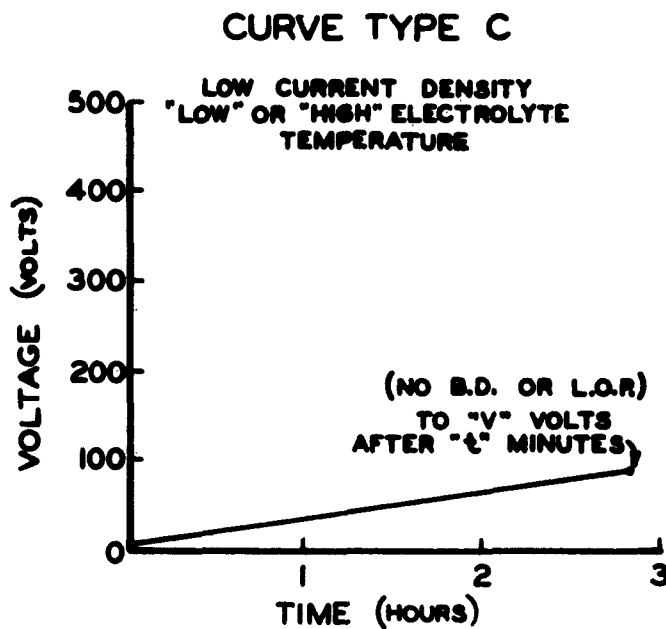
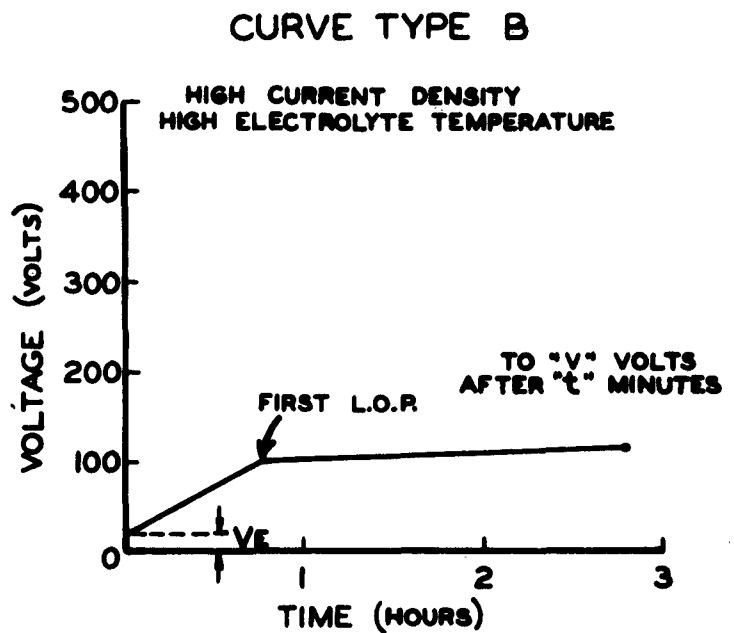
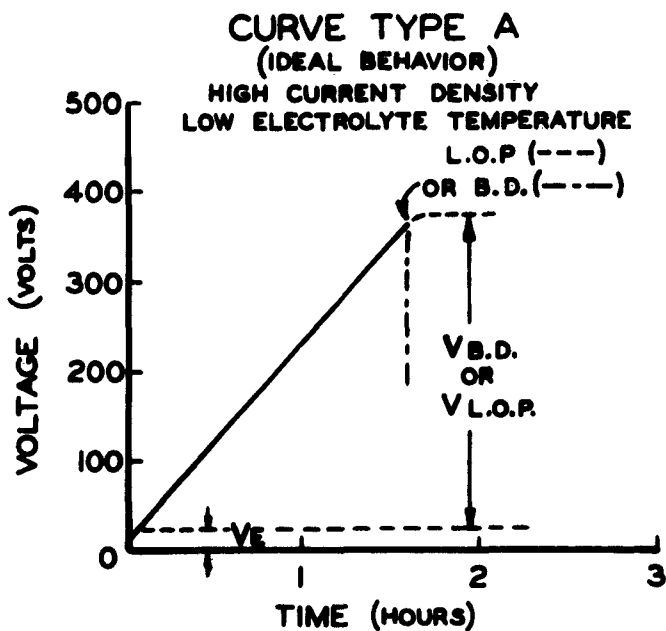


FIG. III
LEAKAGE CURRENT vs. TIME AT FORMATION VOLTAGE

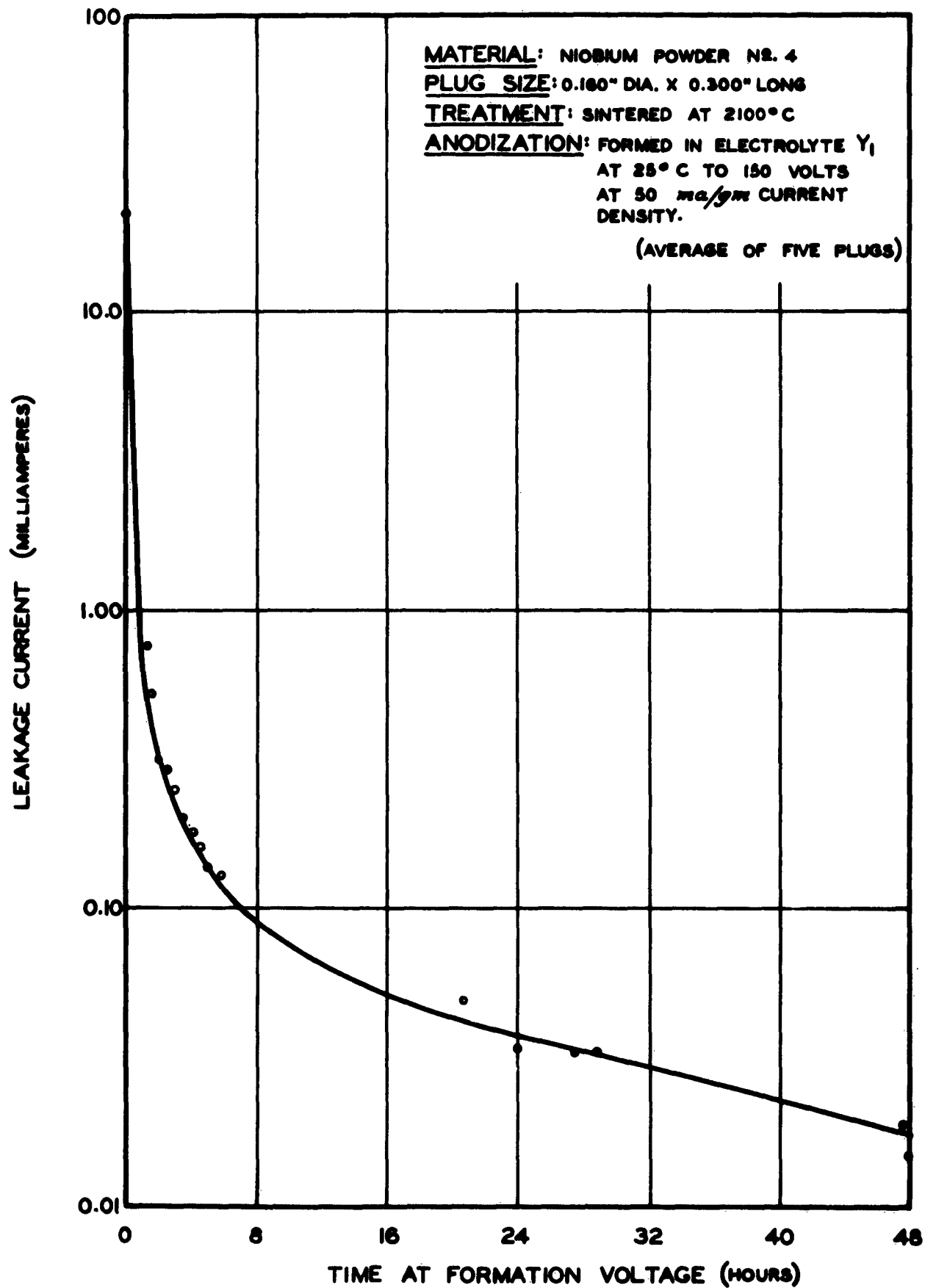
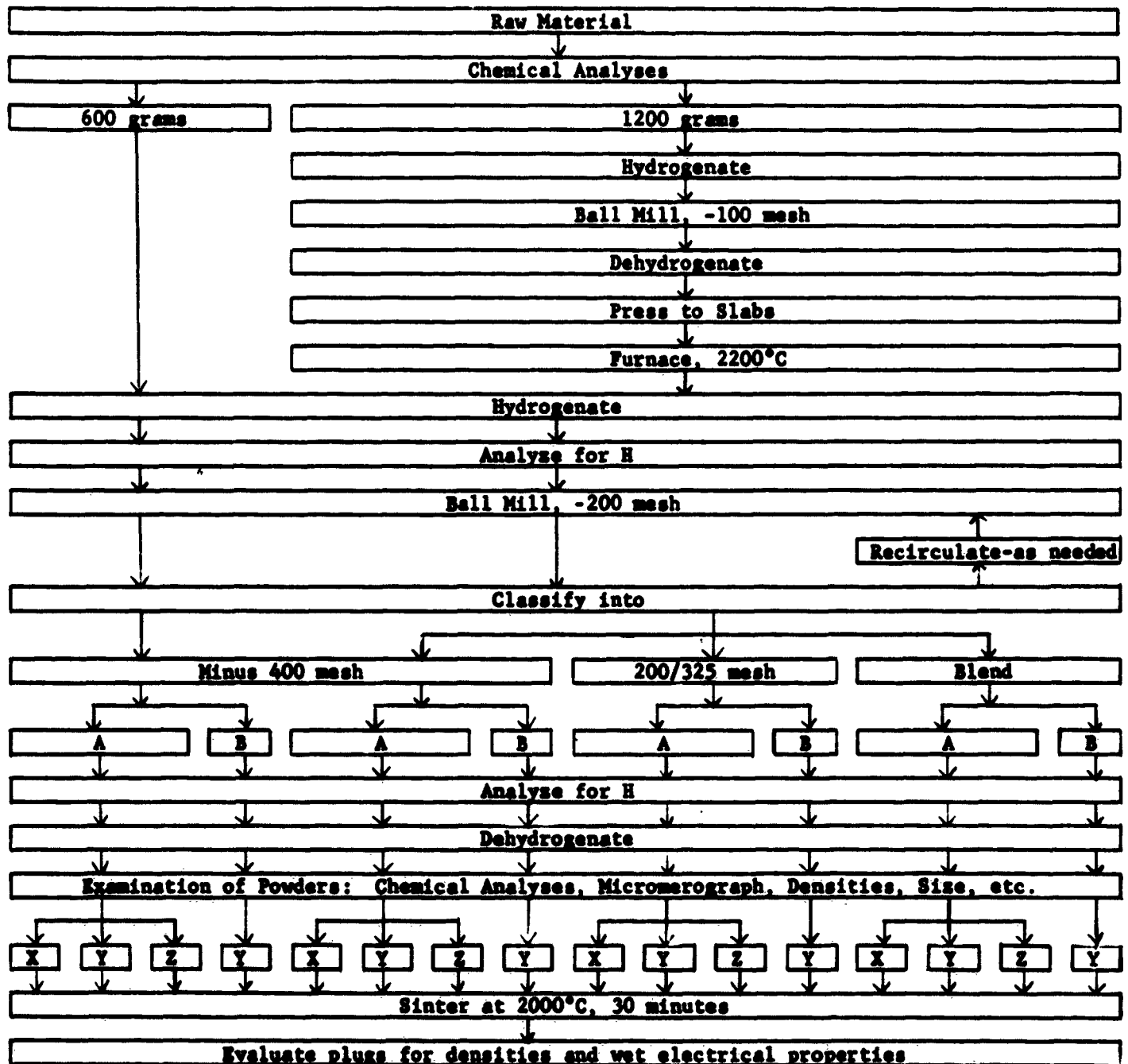


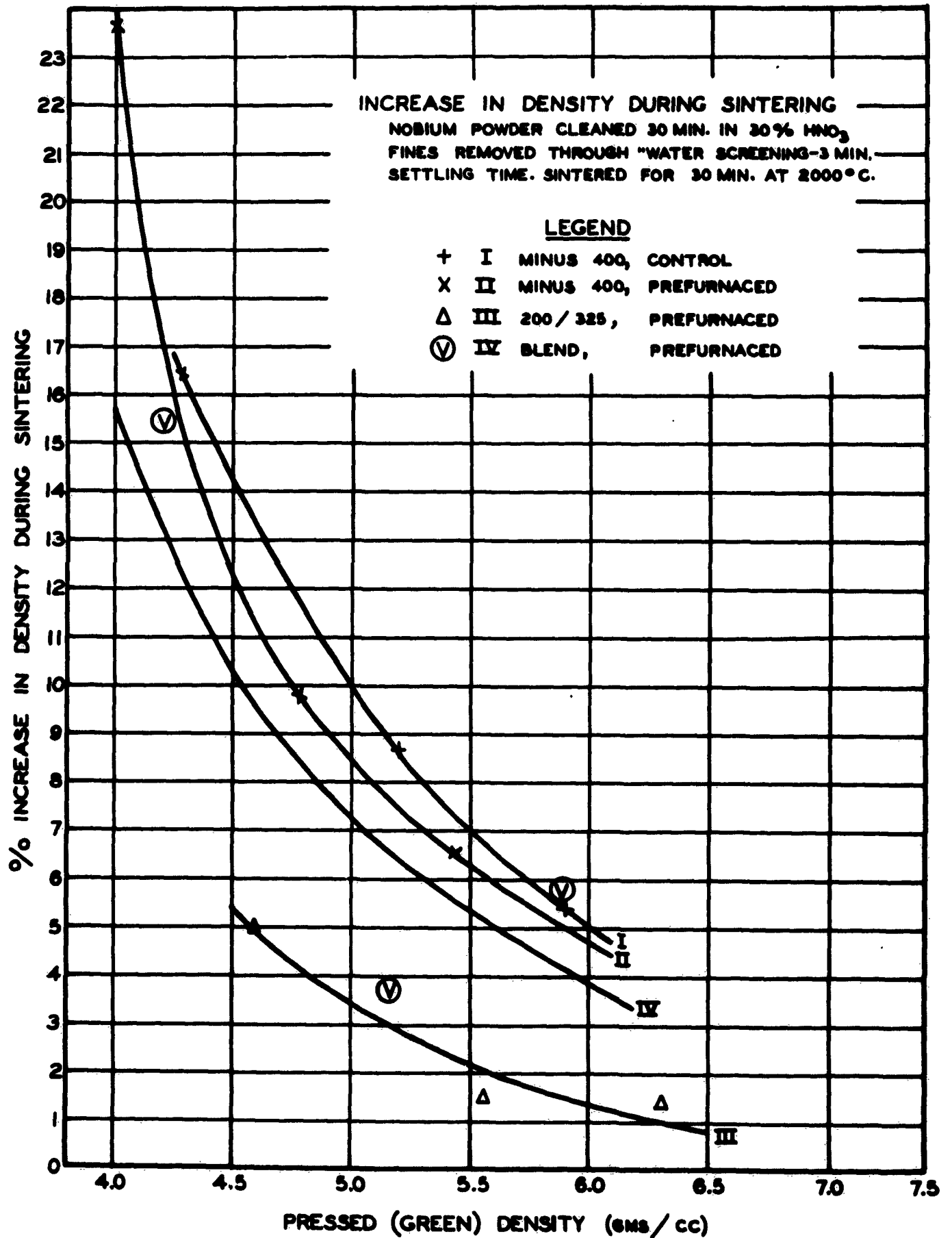
FIGURE IV
CLASSIFICATION OF NIOBIUM POWDERS



LEGEND:

- A - Clean 30 minutes in 30% HNO₃, remove fines through "water screening".
- B - Etch 60 minutes in 10% Br in methanol, wash.
- X - Press plug to minimum green density.
- Y - Press plug to minimum +0.75 gm/cc.
- Z - Press plug to minimum +1.50 gm/cc.

FIG. V



FLOW DIAGRAM FOR IMPREGNATION-REFORMATION STUDIES ON NIOBIUM SINTERED PLUGS



‡: Number of Na(MO₃)₂ dips.
*: No pre-impregnation treatment.
N₀: Minimum number of dips to give

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